ELSEVIER

Catalysis Today 42 (1998) 117–125

CATALYSIS TODAY

Catalytic properties of Cu on sulphated zirconias for $DeNO_x$ in excess of oxygen using *n*-decane as reductant

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Abstract

The selective catalytic removal of NO by decane, in oxygen rich atmosphere has been investigated on Cu/sulphated zirconia catalysts. The introduction of Cu using $Cu(acac)_2$ in organic solvent results in well dispersed Cu^{2+}, and little change of acidity of the carrier. In absence of sulphate on the support a linear correlation between catalytic activity and the reducibility of Cu ions can be obtained from previous results. By contrast, for Cu/SZ catalysts, $DeNO_x$ obeys a bifunctional mechanism. The activity per exposed Cu atom is constant at low temperature whatever the acidity of the support, showing that the rate determining step is then controlled by copper. Above 600 K the turnover frequency increases with the amount of sulphur on the support, showing that the slow step is now an acid catalysed reaction. Water has only a reversible effect on activity. The largest inhibition is due to SO_2: adding 20 ppm of SO_2 to the feed results in a fourfold decrease of rate. This inhibition is sensitive to the dispersion of Cu: poorly dispersed catalyst obtained by impregnation, are not inhibited by sulphur dioxide, and a compromise must then be found between activity and thioresistance.

Keywords: $DeNO_x$; Diesel exhaust gases; Selective reduction; Decane; SO_2 poisoning; Copper oxide; Sulphated zirconia; Turnover frequency

1. Introduction

The elimination of NO_x in the exhaust gases of diesel and lean-burn engines requires the selective catalytic reduction (SCR) of NO to N_2 in the presence of excess O_2. The mechanism of this process is complex and depends on the catalyst [1], the type of hydrocarbon [2] and reaction conditions [3]. Several recent results point out the promoting effect of acidity on the activity and selectivity of the reaction [4–8]. For the SCR of NO by decane, N_2 was selectively formed over Cu/ZrO_2 at reaction temperatures below 573 K, while NO_2 was the main product above 673 K. Over Cu on sulphated zirconia (SZ) this reaction became selective to N_2 up to 773 K [4]. For the SCR of NO by methane, Loughran and Resasco [8] have shown that SZ added in mechanical mixtures to Pd/SiO_2 promoted the activity. For the SCR of NO by decane, the addition of SZ to copper manganite shifted the products of reaction from NO_2 on pure Cu manganite to N_2 with the mechanical mixture [5]. These observations prove that the reaction can proceed on different sites located on the oxide phase and on the acid support, and follows then a bifunctional path.

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0920-5861/98/$32.00
PII S0920-5861(98)00082-0

Various reaction schemes have been proposed in addition to the redox mechanism involving the Cu^{+} generated by reduction of the Cu^{2+} cations [9], which is the predominant path on supported Cu catalysts in absence of sulphur [10]. In particular several bifunctional mechanisms have been forwarded where:

1. NO is oxidised to NO_2 at the metal oxides or cationic sites, followed by the reaction of NO_2 with an adsorbed hydrocarbon activated by the acid function [11,12].
2. Hydrocarbons are converted to some intermediate reacting with NO_x [13,14].
3. NO is oxidised to NO_2 and the hydrocarbon oxidised to aldehyde on the Cu oxide phase, followed by the nitration of the aldehyde by NO_2, and further decomposition of the resulting nitro compound to N_2 [5]. This proposal is based on the fact that aldehydes can be nitrated by acid catalysis at room temperature [15], and accounts for the activity of pure solid acids in SCR of NO, in a temperature range where aldehydes could be formed by the gas phase oxidation of hydrocarbons [16–22].

It thus appeared interesting to change the sulphur and copper content of Cu/SZ catalysts, in order to investigate the effect of the acidity of the support and of redox properties of Cu on the SCR of NO by decane in O_2 rich atmosphere. Moreover, these $DeNO_x$ catalysts are known to be sensitive to poisoning by sulphur contained in the fuel, and thioresistance is then of practical importance, but has been scarcely studied [23–25]. It was earlier reported that SO_2 promoted and not inhibited the activity of Cu/ZrO_2, and its effect is studied here on Cu/SZ.

2. Experimental

2.1. Catalyst preparation

Zirconium hydroxide was obtained by precipitation of zirconia from a $ZrOCl_2.8H_2O$ (Fluka) solution at a constant pH=10. The precipitate was filtered, washed chloride-free and dried overnight at 393 K. The SZ samples were prepared by contacting dried $Zr(OH)_4$ with a H_2SO_4 solution. After filtering, the solid was dried overnight at 393 K.

Cu catalysts were obtained by contacting for 6 h, 3 g of the support (ZrO_2 or SZ), dried overnight at 473 K under He, with an adequate amount of copper acetylacetonate (Janssen) in 200 cm^3 of acetylacetone solution (Prolabo) as described by Boitiaux et al. [26] for noble metals. The solid was filtered, dried at 393 K for 3 h, then calcined under air at 773 K for 3 h. The sulphur and copper contents were varied from 1 to 8 wt%. The labelling of the sample, e. g., Cu(3)/SZ(5.3), means that this sample contains 3 wt% Cu and 5.3 wt% S. A Cu/MFI supplied by IFP (Si/Al=27.0) formerly proved to be very efficient in the SCR of NO by propene and propane [11] was used for comparison purpose.

2.2. Catalyst characterisation

The catalysts were characterised by chemical analysis (Laboratoire d'analyse du CNRS, Vernaison, France), nitrogen sorption at 77 K (Micromeritics ASAP 2000), X-ray diffraction (CGR Theta 60 instrument using CuKα monochromated radiation), temperature programmed desorption of acetonitrile (TPD), temperature programmed reduction by H_2 (TPR) and temperature programmed oxidation by oxygen (TPO) and electron spin resonance.

The acid properties of the samples were evaluated by TPD of CH_3CN using the procedure previously reported [27]. An aliquot of the catalyst ($\approx$0.100 g) was reactivated in situ at 673 K for 1 h under air. After saturation of the sample with CH_3CN at room temperature, physisorbed CH_3CN was removed by treatment under N_2 at 363 K. CH_3CN desorption was then started under nitrogen flow (50 cm^3 min^{-1}) from 363 to 823 K at 6 K min^{-1}. CH_3CN released in the carrier was analysed by sampling on line every minute to a gas chromatograph.

The reducibility of copper species by H_2 was determined by TPR as described elsewhere [28] using H_2/Ar gas (3/97, vol/vol, purity of both gases > 99.95%) and linear temperature programation between 293 and 873 K (ramp: 5 K min^{-1}, flow: 20 ml min^{-1}). The experimental set-up of TPO was similar with O_2/He: 3/97, and high purity gases (>99.995%). The standard cycle applied to the sample was: (1) H_2 TPR up to 650 K, (2) O_2 TPO up to 650 K and (3) H_2 TPR up to 1173 K. The nature of Cu species, in Cu/SZ catalysts, was identified by electron spin resonance (ESR) experiments.

2.3. Catalytic properties

The SCR of NO by decane was performed in a flow reactor operated at atmospheric pressure. An aliquot (≈0.050 g) of the powdered catalyst was activated in situ at 673 K for 1 h under air. After flushing with He, the reactor was cooled down to room temperature. The reaction was performed using a gas mixture containing 0.1 vol% NO (purity > 99.995%), 0.03 vol% *n*-decane (purity > 99.5%) and 9 vol% O_2 (purity > 99.995%) in helium. The flow rate was 60 ml min^{-1} (space velocity 70 000 h^{-1}) and the temperature from 298 to 750 K (ramp: 5 K min^{-1}). Several measurements were done at the stationary state to determine the turnover frequencies. In the absence of SO_2 the activity was found constant for at least 24 h at 723 K, then deactivation was considered as negligible. The effect of SO_2 (20 ppm) and water (2 vol%) were determined at the stationary state.

The composition of the effluents was monitored continuously by sampling on line to a quadrupole mass spectrometer Balzers QMS 421 equipped with a Faraday detector (0–200 amu) and following the masses 28, 30, 44, 46 and 57. Nitrogen and carbon monoxide formations were discriminated by analysing the products with a gas phase chromatograph (Varian) equipped with a katharometer and a 13 X molecular sieve column.

3. Results

3.1. Characterisation of the catalysts

The surface areas and dispersion of Cu determined by NO desorption, for the solids used in the present work are reported in Table 1. The BET surface area retained after calcination at 773 K is affected by the amount of sulphur, and reaches a maximum at a content of 2.5–3.5%. The introduction of about 4% Cu does not alter significantly the surface area. The dispersion of Cu decreases with the Cu% introduced, and also with the acidity of the support. Therefore the process of deposition of Cu is probably not a reaction of the Cu salt with the acid sites, but a simple adsorption.

The desorption of CH_3CN from the present series of catalysts shows two peaks at around 400–420 K (LT)

Table 1
Some physico-chemical characteristics of the samples

Catalysts	Amount of CH_3CN desorbed (mmol m^{-2})			BET surface area (m^2 g^{-1})	NO/Cu[a] (mol mol^{-1})
	Total	Under LT	Under HT		
$Zr(OH)_4$	—	—	—	290	
ZrO_2	—	—	—	134	
SZ(1.0)	1.3	0.7	0.6	182	
SZ(1.4)	1.5	0.8	0.7	187	
SZ(2.5)	2.0	0.9	1.1	207	
SZ(3.5)	2.2	1.1	1.1	205	
SZ(5.3)	1.7	1.1	0.6	160	
Cu(3.7)/ZrO_2	0.9	0.5	0.4	136	0.42
Cu(3.0)/SZ(1.0)	0.9	0.7	0.2	174	0.59
Cu(3.0)/SZ(1.4)	1.1	0.7	0.4	163	0.55
Cu(4.0)/SZ(2.5)	1.7	1	0.7	230	0.34
Cu(3.9)/SZ(3.5)	2.1	1.2	0.9	222	0.26
Cu(3.0)/SZ(5.3)	1.6	1.2	0.4	158	0.15
Cu(0.8)/SZ(3.5)	2.3	1.4	0.9	215	0.57
Cu(3.2)/SZ(3.5)	2	1.1	0.8	222	0.29
Cu(7.9)/SZ(3.5)	2	1.6	0.4	147	0.08

[a]From [34].

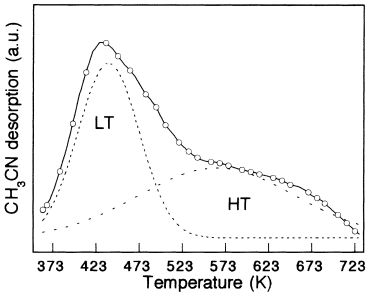

Fig. 1. Example of CH_3CN TPD profile: SZ(2.5).

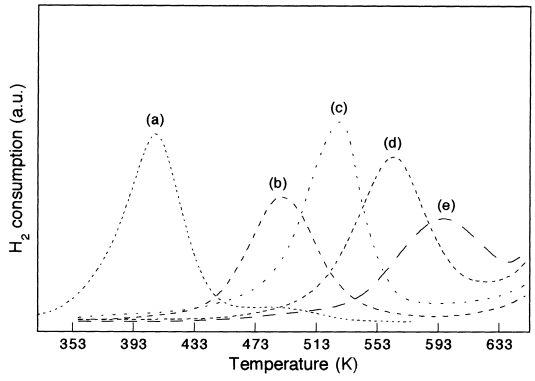

Fig. 2. H_2 TPR profiles of: (a) $Cu(3.7)ZrO_2$, (b) Cu(3.0)SZ(1.4), (c) Cu(4.0)SZ(2.5), (d) Cu(3.9)SZ(3.5) and (e) Cu(3.0)SZ(5.3).

and 550–600 K (HT) (Fig. 1). The total amount of CH_3CN desorbed increases up to a sulphur content of 3.5% and then decreases (Table 1). The respective amounts of CH_3CN desorbing under the LT and HT peaks follow the same behaviour. If we accept that a surface sulphate species occupies about 2.5 nm^2 [29], the monolayer on a zirconia surface of 200 $m^2\ g^{-1}$, corresponds to a sulphur content around 4.0 wt%. As expected for an impregnation in organic medium the deposition of copper on SZ(3.5) modifies little the total acidity of the support. The main change is the increase of the weak acidity at the expense of the strong acidity.

No diffraction line of a CuO phase was detected on zirconia-supported Cu catalysts. The absence of hyperfine structure in the ESR spectrum of Cu(3.9)SZ(3.5) rules out the presence of isolated Cu^{2+} species. Cu is then most likely in the form of a disordered copper oxide phase.

3.2. *TPR study of* Cu *ions*

The redox properties were investigated by TPR/TPO. In our conditions, ZrO_2 did not show any reduction peak below 900 K. The reduction of sulphate species in SZ started at around 773 K with a peak maximum in the range 823–873 K. The reduction profile of copper-containing samples shows a reduction peak at low temperature attributed to Cu reduction. The presence of Cu induced a temperature shift, by 100–130 K to lower values, of the peak of sulphate species, as observed in the TPR of SZ-supported Ni and Pt [30,31].

The TPR profiles of Cu/ZrO_2 exhibits a single peak with a maximum at 409 K (Fig. 2), which denotes an easy reduction of CuO/ZrO_2. The reducibility of copper on Cu/SZ, assessed from the temperature (T_m) of the TPR peak, decreases monotonously with the increase of sulphur content. From the H_2 uptake, H_2/Cu, varying between 0.84 and 1.1 (Table 2) it can be concluded that copper species are reduced to Cu^0 before sulphate reduction becomes significant. The copper loading has only a small effect on the TPR spectra at constant sulphur content.

It was earlier reported [10] that the reoxidation of the surface is much faster and occurs at lower temperature (Table 2). The temperature T_{m2} of the reoxidation peak is shifted to higher values with the sulphate content of the catalyst. An increase of the Cu content, decreased both the reducibility and oxidability of Cu species.

3.3. *Catalytic properties*

No activity was detected on ZrO_2 or SZ below 773 K at a HSV of 70 000 h^{-1} for the SCR of NO by decane, but ZrO_2 showed a weak NO conversion at higher temperature. Cu/ZrO_2 showed two waves of NO conversion (Fig. 3): (i) the first one around 563 K where NO was selectively reduced to N_2 and (ii) the second at higher temperature (753 K) where NO was mainly oxidised to NO_2. On Cu/SZ, only NO_2 traces were detected in the whole temperature range during the SCR of NO. It is known that SZ develops strong acidity, only after calcination around 923 K [32]. Indeed, calcination of Cu/SZ above 773 K yields a catalyst less active for NO reduction (Fig. 3). It seems therefore that strong acidity is not required for the

Table 2
Quantitative analysis of the TPR by H_2 and the TPO by O_2

Catalysts	TPR by H_2		TPO by O_2	
	T_m[a] (K)	H_2/Cu (mol mol^{-1})	T_m[b] (K)	T_{m2}[c] (K)
Cu(3.7)/ZrO_2	409	1.00	371	465
Cu(3.0)/SZ(1.0)	491	0.91	379	491
Cu(3.0)/SZ(1.4)	489	0.84	379	489
Cu(4.0)/SZ(2.5)	540	0.95	379	507
Cu(3.9)/SZ(3.5)	563	1.10	388	525
Cu(3.0)/SZ(5.3)	599	0.90	391	533
Cu(0.8)/SZ(3.5)				
Cu(3.2)/SZ(3.5)	579	0.86	391	525
Cu(7.9)/SZ(3.5)	562	1.00	410	541

[a]Temperature of faster reduction rate.
[b]Temperatures of faster oxidation rate for the first peak.
[c]Temperatures of faster oxidation rate for the second peak.

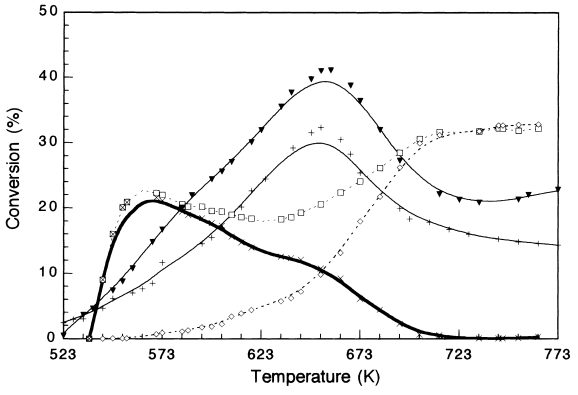

Fig. 3. NO conversion in SCR of NO by decane on: (□) Cu(3.7)ZrO_2; (▼) Cu(4.0)/SZ(2.5) calcined at 773 K and (+) Cu(4.0)/SZ(2.5) calcined at 873 K. NO conversion in N_2 (×) and in NO_2 (◇) on Cu(3.7)ZrO_2.

SCR of NO. However, as evidenced in Table 3, the increase of sulphate content favours the reduction to N_2 above 623 K, and shifts the maximum conversion of NO to higher temperatures.

The oxidation of decane produced essentially CO_2, with only trace amounts of CO detected below 673 K. The oxidation started around 523 K, at lower temperatures than the NO reduction. The presence of sulphate shifted this temperature by 20–30 K towards higher temperature (Fig. 4). Table 3 reports the NO conversion in N_2 at 573, 623, and 673 K for all the catalyst studied. It is clear that NO reduction is enhanced by sulphur and reaches a maximum for a sulphate coverage close to the monolayer (3.5 wt%). A small amount (0.8 wt%) of Cu deposited on ZrS(3.5) is enough to induce NO conversion below 773 K. The best results are observed for Cu(3.2)/SZ(3.5). The temperature where the conversion of NO to N_2 is maximum and the temperature at which hydrocarbon oxidation starts decreases as the amount of copper increases.

3.4. *Deactivation by* SO_2 *and water*

These compounds are well-known inhibitors of the activity of Cu catalysts and their effect was investigated, introducing 20 ppm of SO_2 and 2 vol% of water in the feed, with HSV increased to 140 000 h^{-1}. Water has a negative effect on activity, but the conversion remains constant as a function of time. This corresponds to a kinetic effect and not to sintering or hydrolysis of sulphates. In Table 4, Cu on pure and sulphated zirconia, and MFI are compared. The addition of water to the feed decreases the conversion by a factor of 2, but does not change much the temperature of the maximum of activity. In presence of 2% water Cu/ZrO_2 is more active than Cu on sulphated zirconia.

SO_2 is a stronger inhibitor and reduces the activity by a factor of 4. A synergy between water and SO_2 appears on Cu/MFI but this effect is not observed on Cu/SZ. It can be pointed out that we reported before that Cu supported on zirconia, sulphated by SO_2 in the

Table 3
Results of the SCR of NO by decane

Catalysts	Conversion of NO to N_2 (%)			Maximum of NO conversion	
	573 K	623 K	673 K	Temperature (K)	Conversion (%)
$Cu(3.7)/ZrO_2$	22	13	6	558	22
Cu(3.0)/SZ(1.0)	18	27	15	623	27
Cu(3.0)/SZ(1.4)	17	25	17	642	29
Cu(4.0)/SZ(2.5)	17	31	35	653	40
Cu(3.9)/SZ(3.5)	20	34	38	653	45
Cu(3.0)/SZ(5.3)	8	6	14	683	20
SZ(3.5)	0	0	0	—	—
Cu(0.8)/SZ(3.5)	0	3	7	738	28
Cu(3.2)/SZ(3.5)	13	26	33	655	38
Cu(7.9)/SZ(3.5)	12	28	18	634	38

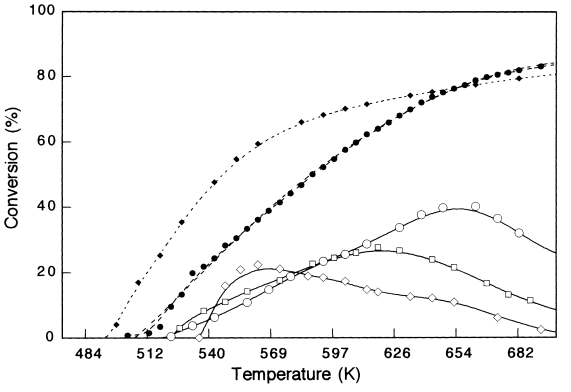

Fig. 4. Effect of sulphur content in SCR of NO by decane on copper zirconia catalysts: $Cu(3.7)ZrO_2$ – (◇) NO conversion in N_2 and (◆) decane conversion in CO_2; Cu(4.0)/SZ(2.5) – (○) NO conversion in N_2 and (●) decane conversion in CO_2; Cu(3.0)/SZ(5.3) – (□) NO conversion in N_2.

gas phase was not poisoned by SO_2 [10]. The Cu loading of these solids was rather high (4.2%) and particles larger than 4 nm could be detected by XRD, thus proving a low dispersion of copper. The effect of the dispersion of Cu on thioresistance was then investigated on a catalyst obtained by the impregnation of a commercial sulphated zirconia (obtained from MEL, surface area 100 $m^2\ g^{-1}$) by Cu nitrate solution using the method of incipient dryness. NO adsorption gives a dispersion of 2% for Cu in that case. As illustrated in Fig. 5 this sample shows a remarkable thioresistance.

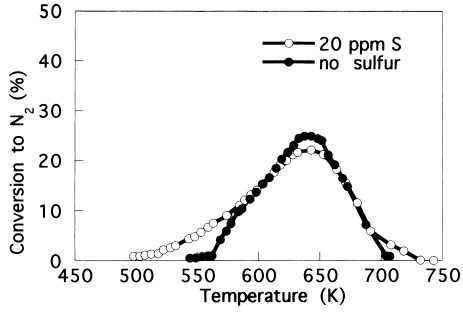

Fig. 5. Effect of SO_2 on the selective reduction of NO by decane over a poorly dispersed Cu on sulphated zirconia catalyst (HSV=140 000 h^{-1}).

Table 4
Maximum conversion of NO, and corrresponding temperatures for Cu on different supports, in the absence or the presence of sulphur dioxide and water

Solid	NO		$NO+SO_2$		$NO+H_2O$		$NO+SO_2+H_2O$	
	T_M	(%)	T_M	(%)	T_M	(%)	T_M	(%)
Cu/ZrS	639	23	658	6	633	10	648	5.5
Cu/Zr	—	—	—	—	573	10	—	—
Cu/MFI			708	34	—	—	683	18

4. Discussion

Model CuSZ catalysts in which the Cu and sulphate contents can be changed independently in a wide range can then be obtained by using $Cu(acac)_2$, as precursor. As expected, the doping of ZrO_2 by sulphate improves the acidity of the solid, but this acidity is not greatly modified by Cu addition. The acid properties of pure sulphated zirconias and of Cu/SZ are maximised at a S content close to a theoretical monolayer of sulphate, i.e. 3–4% for 220 $m^2\ g^{-1}$. For higher S loadings, polysulphates are likely to be formed, and Morterra et al. [33] reported earlier that these species are less acidic than sulphates.

From ESR spectroscopies and TPR experiments on these solids, Cu is present under the form of X-Ray amorphous aggregates of CuO. Even the Cu(7.9)SZ(3.5) sample of low accessibility of Cu to NO (NO/Cu=0.08) did not show any X-Ray diffraction pattern. This low accessibility observed at high S content can be due, in part, to the coverage of the CuO aggregates by sulphates [34].

It was earlier reported that the reducibility of Cu was decreased by the presence of sulphate [10]. Indeed, upon addition of 5.3 wt% S, the reduction peak shifted here by 190 K to higher temperatures. FTIR studies of NO adsorption on CuSZ show a shift of ν(NO) by 38 cm^{-1} to higher frequencies in presence of sulphates (33), and the sulphates species can then be assumed to decrease the reducibility of Cu^{II} by an electron withdrawing effect. A similar explanation was proposed for the lower reducibility of Ni and Pt in SZ [30,31]. The presence of Cu also shifted to lower temperatures the reduction of sulphates.

In the experimental conditions used here (300 ppm of decane as reductant), $Cu(4.0)/ZrO_2$ is active and selective in NO reduction by *n*-decane up to 573 K with a maximum at 558 K. Above 573 K, NO_2 is detected and the catalyst becomes fully selective in NO_2 at 718 K with a conversion reaching 33%. For co-precipitated copper–zirconia oxide catalysts, Bethke et al. [35] observed a maximum of conversion in NO SCR by propene at 561 K for a catalyst containing 6.0 wt% of copper. The high reactivity and selectivity of low loading Cu–Zr–O was attributed to a good dispersion of copper on zirconia. Indeed, for the SCR by decane, the activity of a series of Cu catalysts supported by different non-sulphated supports, including alumina, silica, zirconia or zeolites, increased with the reducibility of Cu, which is also related to its dispersion [10]. Assuming that the reducibility is measured by the temperature of the TPR peak, and catalytic activity by the temperature for 20% conversion, a linear relation is indeed observed (Fig. 6). This correlation could be expected if the slow step is related to a redox reaction catalysed by Cu. However the correlation does not hold in presence of sulphur, since Cu/SZ is less reducible and more active than Cu/ZrO_2. This observation was attributed to the intervention of an acid catalysed reaction.

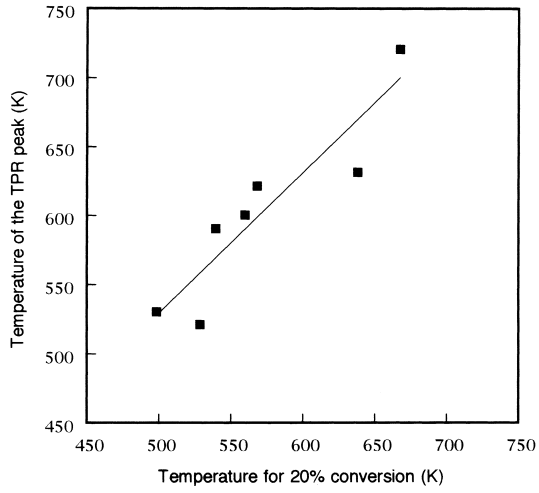

Fig. 6. Relation between reducibility, estimated by the temperature of the TPR peak, and activity measured by the temperature for 20% conversion, of a series of Cu catalysts supported on non-sulphated supports.

The pre-sulphatation of zirconia leads to Cu/SZ catalyst selective for the conversion of NO to N_2 in the whole range of temperatures, and it is then interesting to check whether the variations of the rate with the acidity of the solid are compatible with a bifunctional mechanism formerly developed for reforming [36]. The turnover numbers (TON) for NO reduction in N_2 (activity per Cu site as determined by TPD of NO) at 537, 623 and 673 K are reported as a function of the sulphur content in Fig. 7. At 573 K, the TON remain close to 2.8 h^{-1} whatever the sulphur content. Therefore, acidity does not play a significant role at this temperature, and the overall reaction is controlled by Cu. At 623 and 673 K, the TON goes through a maximum at 3.5% wt sulphur content and then

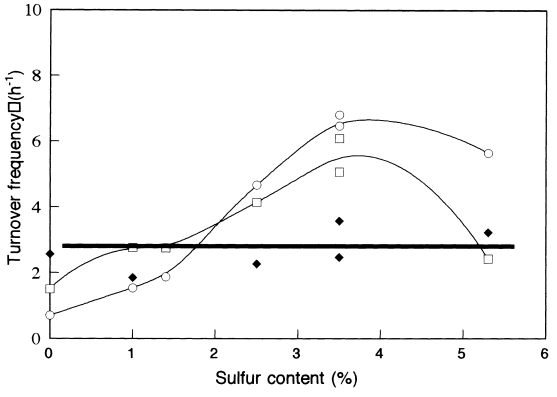

Fig. 7. Effect of sulphur content on the TON of the SCR of NO to N_2 by decane of Cu(3–4)/ZS(y) catalysts at: (◆) 573 K, (□) 623 K and (○) 673 K.

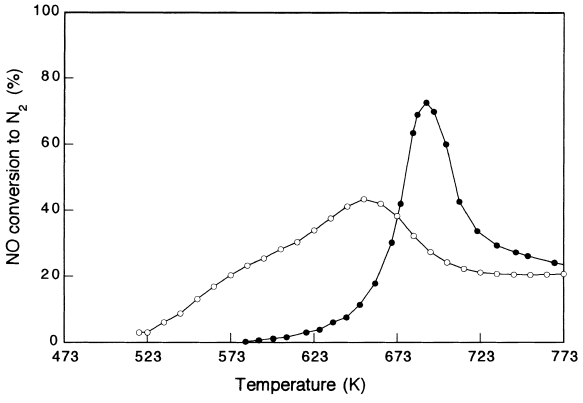

Fig. 8. NO conversion in SCR of NO by decane on Cu(80)-ZSM5(27) (filled points) and Cu(3.9/SZ(3.5) (open points).

decreases. This maximum of activity is reached with an amount of sulphur of 3.5% which corresponds to the maximum acidity. The parallelism of the reaction rate with acidity now shows that, at this higher temperature, the oxidation is fast and the rate is now controlled by the acid function.

The reaction involved in this acid step must involve a product of the oxidation of *n*-decane, since the oxidation of the hydrocarbon starts first, most probably yielding aldehydes or ketones as is known for CuO catalysis. SZ alone is inactive below 773 K whatever the amount of sulphur, but becomes active at higher temperatures, where the hydrocarbon can be oxidised in the gas phase by radical mechanisms. Cu/ZrO_2 yields NO_2 [4] and the mechanism going through the oxidation of NO to NO_2 in the first step followed by nitration of a product of the oxidation of the hydrocarbon in a second step can be proposed. Carbonylic compounds which can be nitrated at low temperature would be good candidates for this purpose, and the resulting nitro-organic compound could be decomposed to N_2 and CO_2 through different surface intermediates [37]. The acid properties generated by impregnation of sulphates onto zirconia must drastically enhance nitration and therefore are essential to maintain the selectivity in N_2 above 600 K for Cu/ZrO_2 catalysts.

In a bifunctional mechanism, Cu/SZ and Cu/MFI should show similar properties, since both consist of Cu on a strongly acidic support. The reaction profiles of Cu(80)MFI and Cu(3.9)/SZ(3.5) are compared in Fig. 8 using the same experimental conditions. Cu(80)MFI is indeed more active but offers a narrower temperature window than Cu(3.9)/SZ(3.5). Cu/SZ shows a higher activity at a lower temperature of 623 K, which may be of practical interest. It can be pointed out also that these Cu/SZ catalyst show a good stability as a function of time, and are therefore not irreversibly deactivated like MFI, by the water produced in the reaction.

They are also thioresistant, when the dispersion of Cu is low enough. Sulphur dioxide is an acid reagent, which should interact with basic sites. The lower resistance of well dispersed Cu oxide agrees with the descriptions of the basicity of oxides. It has been demonstrated for MgO and CaO that basicity increases with the surface area of the sample, and basic sites have been identified to defects, more numerous on small crystals i.e. at high surface area [38,39]. At 573 K the turnover frequency is constant for Cu loadings >3%, then the activity is proportional to the CuO surface. A compromise has then to be found between activity and thioresistance for a use in presence of sulphur.

In conclusion in the absence of SO_2 in the feed, an adequate balance between acidity and redox properties of Cu/SZ generates a catalyst which is efficient and selective for the SCR of NO by decane in the presence of oxygen. The maximum acidity was obtained by deposition of a sulphur content close to that required to form a monolayer. In this catalyst, copper oxide is highly dispersed, in strong interaction

with sulphate species and more difficult to reduce. Acidity plays a crucial role by maintaining complete selectivity to N_2 in the whole range of temperature, and the effect on activity is greater at high temperature. The $DeNO_x$ activity is very sensitive to trace amounts of SO_2 and thioresistance strongly depends of the dispersion of Cu oxide.

Acknowledgements

The support of this work by the European Union Community (BRITE EURAM II contract No. BRE2-CT92-0192) is gratefully acknowledged. DT thanks The Institut Français du Pétrole for a Ph.D. grant.

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